WO 2005/005504 PCT/EP2004/007354

## Claims

5

10

15

1. A composition comprising:

- (A) a dispersion of a crosslinkable polyurethane polymer in aqueous medium, and obtainable from a polyurethane prepolymer which is the reaction product of:
- (i) at least one polyisocyanate, and
- (ii) at least one organic compound containing at least two reactive groups which can react with isocyanates, and
- (iii) at least one compound which is capable to react with an isocyanate group and which contains at least one additional functional group which is susceptible either to dispersion in water and/or to a crosslinking reaction
- in an oxygenated solvent selected from the coalescing agents having a higher boiling point of from 150 to 250°C, under 760 mm Hg and being chemically inert towards isocyanates during the manufacture of the polyurethane;
  - the so obtained polyurethane prepolymer being further neutralised and dispersed in water, and optionally then reacted with a chain extender or capping agent (v) having or not remaining functional groups after the capping;
- 20 (B) a crosslinker which is a vinyl-type polymer having functional groups reactive with the functional groups of the polyurethane polymer (A).
- A composition according to claim 1, wherein said oxygenated coalescing solvent (iv) is selected from the fully reacted alkyl or aryl esters of aromatic, aliphatic or cycloaliphatic polycarboxylic acids, the fully reacted alkyl or aryl esters of aromatic, aliphatic or cycloaliphatic polyglycols, the fully reacted alkyl or aryl ethers of aromatic, aliphatic or cycloaliphatic polyglycols, the fully reacted mixed alkyl and aryl esters and ethers of mixed aromatic, aliphatic or cycloaliphatic polyglycol-carboxylates, the unsubstituted and alkyl and aryl substituted cyclic carbonates, the unsubstituted and alkyl and aryl substituted cyclic ethers, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic esters, the unsubstituted and alkyl and aryl substituted cyclic anhydrides.
- 3. A composition according to claim 2, wherein said oxygenated coalescing solvent (iv) is selected from dimethyl esters or dissobutyl esters of adipic, glutaric, succinic or phtalic acids, ethyl-3-ethoxypropionate, 2,2,4-trimethyl-1,3-pentanedioldiisobutirate, ethylene carbonate, propylene carbonate, propyleneglycol diacetate and dipropylene glycol dimethyl ether, alone or in admixture.

WO 2005/005504 PCT/EP2004/007354

37

- 4. A composition according to any of claims 1 to 3, wherein said coalescing solvent (iv) is used in an amount of 5 to 40 weight % expressed on the dry polymers.
- 5 S. A composition according to any of claims 1 to 4, wherein the polyisocyanate (i) is an aliphatic, cycloaliphatic, aromatic or heterocyclic polyisocyanate or a combination thereof.
- 6. A composition according to any of claims 1 to 5 wherein the organic compound (ii) containing at least two isocyanate-reactive groups is selected from the group consisting of polyester polyols, polyether polyols, polycarbonate polyols, polyacetal polyols, polyesteramide polyols, polyacrylate polyols and polythioether polyols, alone or in admixture.
- 7. A composition according to any of claims 1 to 6, wherein the isocyanate-reactive compound (iii) contains at least one anionic salt functional group or acid group which may be subsequently converted to such anionic salt group, and is (a) a hydroxycarboxylic acid of general formula (HO)<sub>x</sub>R(COOH)<sub>y</sub>, wherein R represents a straight or branched chain hydrocarbon radical having 1 to 12 carbon atoms,
  20 and x and y are integers from 1 to 3, or (b) a sulfonated polyester obtained by the reaction of a sulfonated dicarboxylic acid with one or more polyhydric alcohols, or by the reaction of a sulfonated diol with one or more polycarboxylic acids.
- 8. A composition according to any of claims 1 to 7, wherein the capping agent (v) is water or an aliphatic, alicyclic, aromatic or heterocyclic primary or secondary polyamine having up to 80 carbon atoms which can bear a further functional group such as in gamma-aminopropyltrimethoxysilane, gamma-aminopropyltriethoxysilane, N-beta-aminoethyl-gamma-aminopropyltrimethoxysilane, bis-(gamma-trimethoxysilylpropyl) amine and N-beta-(aminoethyl)-gamma-aminopropylmethyldimethoxysilane.
- A composition according to any of claims 1 to 8, wherein the vinyl-type polymer is the product formed by the free-radical addition polymerization of at least one monoethylenically unsaturated monomer with at least one other ethylenically unsaturated monomer containing a functional group such as an acetoacetoxyalkyl ester group, carboxylic and sulfonic groups, isocyanates, hydroxy, amine, acrylic, allylic, vinyl, alkenyl, alkinyl, halogen, epoxy, aziridine, aldehyde, ketone, anhydride, carbonate, silane, carbodiimide, ureidoalkyl, N-methylolamine, N-

methylolamide N-alkoxy-methyl-amine, N-alkoxy-methyl-amide, and capable to provide a crosslinking reaction with the polyurethane component.

10. A composition according to claim 9, wherein the monoethylenically unsaturated monomer containing an acetoacetoxyalkyl ester group is a compound having the formula

$$R^1$$
-O-CO-CH $_2$ -CO-CH $_3$ 

wherein R<sup>1</sup> represents a

10 CH<sub>2</sub>=CR'-COO-R"- group or a CH<sub>2</sub>=CR'-R"- group in which
R' is a hydrogen atom or a methyl radical and
R" is an alkylene radical having 1 to 12 carbon atoms.

- 11. A composition according to claim 10, wherein the monoethylenically unsaturated monomer containing an acetoacetoxyalkyl ester group is acetoacetoxyethyl (meth)acrylate.
  - 12. A composition according to any of claims 9 to 11, wherein the monoethylenically unsaturated monomer containing an acetoacetoxyalkyl ester group is present in an amount of from about 1 to about 80 % by weight of the vinyl polymer.
  - 13. A composition according to any of claims 9 to 12, wherein the monoethylenically unsaturated monomer containing an acetoacetoxyalkyl ester group is present in an amount of from about 5 to 20 % by weight of the vinyl polymer.

25

20

- 14. A composition according to any of claims 1 to 13, wherein the weight ratio of said at least one polyurethane polymer to said at least one vinyl polymer is within the range of from 95:5 to 5:95.
- 30 15. A composition according to any of claims 1 to 14, wherein the weight ratio of said at least one polyurethane polymer to said at least one vinyl polymer is within the range of from 1:2 to 2:1.
- 16. A process for the preparation of an aqueous crosslinkable resin composition
  according to any of claims 1 to 15, which comprises homogenously mixing
  together at room temperature an aqueous dispersion of at least one polyurethane
  polymer and an aqueous dispersion of at least one vinyl polymer

5

- 17. A process for the preparation of an aqueous resin composition according to any of claims 1 to 15, which comprises subjecting the monomers of the vinyl polymer having functional groups to radical polymerisation in the presence of an polyurethane polymer having anionic salt functional groups or subjecting an isocyanate-terminated polyurethane prepolymer having anionic salt functional groups to chain-extension with a capping agent in the presence of a vinyl polymer having functional groups.
- 18. A protective or adhesive coating obtained with an aqueous composition according to any of claims 1 to 17.